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ACIDIC PRECIPITATION IN SOUTH-CENTRAL ONTARIO:

RECENT OBSERVATIONS

September, 1977

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Ministry
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The Honourable
George A. Kerr, Q.C.,
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K.H. Sharpe,
Deputy Minister

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ACIDIC PRECIPITATION IN SOUTH-CENTRAL ONTARIO:

RECENT OBSERVATIONS

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PREFACE

In 1975, an interministerial multidisciplinary study of the effects of recreational and urban development on lakes called the Lakeshore Capacity Study was initiated. The Limnology and Toxicity Section of the Water Resources Branch has conducted studies on the effects of development on water quality. The field surveys involved detailed analysis of the hydraulic and materials budgets of the study lakes. While sampling concentrated on nutrients, a complete set of chemical data was routinely collected on the lake, runoff and precipitation samples.

It became apparent that precipitation acidity was high while lake buffering capacities were low. Since lake acidification has been reported to effect undesirable changes in biotic communities, it was essential that the interaction of acid and development-related nutrient inputs be investigated.

This report describes studies of precipitation chemistry carried out in south-central Ontario in 1976. Information was also drawn from the Sudbury Environmental Study which is concerned with the study of acidified lakes in the immediate Sudbury area.

ABSTRACT

The precipitation in south-central Ontario, with mean pH between 3.95 and 4.38 and frequent event pH's of <4.0 is more acidic than that in the Sudbury region and in Scandanavia, and as acidic as that in the northeastern U.S.A. As in New England, a major component of the total acidity is strong mineral acid. Because most lakes in south-central Ontario have very low buffering capacity (14-200 μeq l^{-1}), high acid loadings are likely to lead to acidification of many lakes and streams in the forseeable future. Although it is not yet possible to estimate the time required for this to happen, there is already some evidence of declining buffering capacity in a few lakes and streams.

INTRODUCTION

Although the occurrence of acidic rain and the resultant acidification of freshwater lakes and rivers has been recognized as a widespread non-localized problem in Scandanavia (Odén 1968, 1975) and in the north-eastern U.S.A. (Likens 1976, Schofield 1976), attention in Ontario has been restricted primarily to the immediate vicinity of Sudbury (Gorham and Gordon 1960, Conroy, Jeffries and Kramer 1974) and to the La Cloche Mountains (Beamish and Harvey 1972, Beamish 1974), about 80 km to the south-west. This is not surprising since Sudbury is the site of the world's largest single point source of sulphur dioxide (Summers and Whelpdale 1975), and the airborne conversion of sulphur dioxide to sulphuric acid is well known (Brosset 1973). Furthermore, the La Cloche Mountains, a series of quartzite ridges of little or no buffering capacity are located in line with one of the prevailing wind directions (Beamish 1976).

A survey of lakes within a 160 km radius of Sudbury has identified lakes with pH <5.5, a level often considered critical for reproductive success of some fish species (EIFAC 1968), as far as 130 km distant in a NNE direction and 60 km in a SSW direction (Conroy, Hawley, Keller and Lafrance 1975). However, many lakes within the immediate vicinity have not been acidified despite significant atmospheric inputs. It is evident that three major factors govern the pH of lakes in the Sudbury area: a) the rate of input of strong acid, b) the location of the lake relative to the prevailing winds (which modifies a), and c) the geochemistry of both the surficial sediments and the bedrock, which determines the buffering capacity of the lake and the runoff waters entering it (Kramer 1975a). The last factor can override all others; that is, calcareous soil or rock can assimilate acidic rain and continue to provide a buffer system for waters located there.

Other parts of Ontario are underlain by silicate bedrock of low solubility and little buffering capacity with only a shallow glacial till overburden, or none at all. Thus, the potential for acidification of lakes in other areas of Ontario exists. One such area of great importance is the Muskoka-Haliburton-Parry Sound-Nipissing region in south-central Ontario (Fig. 1). This note presents preliminary evidence which suggests that acidic rain may cause a severe environmental problem in south-central Ontario.

DESCRIPTION OF STUDY AREA

The portion of Ontario lying east of Georgian Bay, south of Lake Nipissing, and north of the Precambrian Shield-Paleozoic boundary is almost entirely underlain by Precambrian plutonic rock composed of granite, granite gneiss, granite pegmatite and migmatite. Smaller areas of Precambrian sediments and volcanics exist, particularly to the south-east. The overburden of this area consists almost exclusively of shallow till (less than 1m) of acidic Podzols. Exposed bedrock is found frequently. There are, however, localized areas of Precambrian spillways that follow ancient riverbeds, and small areas of sand plains, clay plains and kame moraines. The Paleozoic region to the south consists principally of clastic and carbonate sediments, offering substantially higher buffering capacity. For a detailed discussion of the physiography of the region, see Chapman (1975).

As a result, the many lakes in this region have dilute ionic composition and are weakly buffered. A survey between 1959 and 1962 of 310 lakes throughout Ontario (Ryder 1967) was used to draw isopleths of total alkalinity (Ryder's Fig. 7) for the province. The lakes of the entire region of south-central Ontario were characterized as having <25 mg l^{-1} total alkalinity as $CaCO_3$, with a number of them between 6 and 10 mg l^{-1}. A subsequent survey (Sparling and Nalewajko 1970) of 70 lakes in southern Ontario again demonstrated that lakes in this region were frequently dilute and had total alkalinities of less than 10 mg $CaCO_3 l^{-1}$, with one case (Wren Lake) as low as 3.5.

METHODS

a) Field

Precipitation collectors - Precipitation event samples ("wet" only) were collected using automatic battery-operated, moisture-activated samplers (Applied Earth Sciences Consultants). Samples collected at or near the laboratory site (Dorset, Red Chalk Lake) were analyzed immediately after precipitation events while those more distant were analyzed weekly or less often if no precipitation occured in a given week. Locations are shown in Fig. 1 and periods of operation given in Table 1. One event sampler (Dorset) was modified for winter use by means of an electric light bulb and thermostat kept in the sample compartment. Snow samples were rapidly melted and kept in the liquid state.

Precipitation bulk samples were collected using either 43 cm diameter, 63 cm high polyethylene containers (snow samples) or 10 cm diameter polyethylene funnels with 200 μ Nitex mesh at the base leading into glass bottles (April-November) to prevent contamination by insects. Any obviously contaminated samples were discarded. A bulk collector was set up on the shores of Harp Lake as well as on a raft on the lake.

Rainfall depth was measured using standard 10 cm diameter polycarbonate precipitation gauges.

Lake and Stream sampling - Samples were collected weekly at 2m intervals through the epilimnion of each lake and monthly through the entire water column in the winter with a Van Dorn bottle and weighted according to the volume of the stratum represented prior to chemical analyses. Analyses were carried out for pH and alkalinity within a few hours. On three to six sampling occasions a portion of the sample was fixed with nitric acid for copper, nickel, zinc and manganese analyses, which were usually carried out within a week. Stream samples were collected approximately weekly except in the cases where streams were dry for periods of the summer.

All glassware employed was washed with 2m HCl, rinsed with deionized distilled water at least six times, then rinsed several times in lake or stream water at the sample point. Bottles were filled so that no air bubbles remained when the cap was tightened.

b) Chemistry

pH - Routine pH measurements of precipitation, lake and stream samples were carried out as soon after sampling as possible with a Corning Digital 109 pH meter, after appropriate buffer calibration.

Heavy metals - Copper, nickel, zinc and manganese analyses of acid fixed lake water samples were carried out using standard atomic absorption techniques (Ontario Ministry of the Environment 1975).

Alkalinity - The standard alkalinity determination employed by the Ministry of the Environment involves titration of the samples to a pH of 4.5, i.e. this pH is the assumed equivalence point of the protonation of the bicarbonate ion. This assumption is reasonably good for high alkalinity samples (>4 meq/l) but tends to be an over-estimate for low alkalinity samples, since the equivalence point occurs at pH >4.5. The correct equivalence pH can be determined by using the Gran technique (summarized by Stumm and Morgan 1970). Extrapolation of a plot of (Vo + V) $[H^+]$ vs V to the V-axis intercept (where Vo = volume of sample (ml), V = volume of titrant added (ml), $[H^+]$ = proton concentration (= 10^{-pH})) for $[H^+]$ equivalence proton concentration yields the volume of titrant required to reach equivalence.

Since most of our routine samples were titrated to a fixed endpoint of pH = 4.5, these values are identified as "total fixed-endpoint alkalinities" in the following discussion, while the more meaningful alkalinities determined to the inflection point of the titration curve are termed "total inflection-point alkalinities".

Acidity and Alkalinity Fractionation - Acidity and alkalinity titrations were performed by constant addition of standardized NaOH or H_2SO_4 at 0.1 to 0.4 ml $min.^{-1}$ to a continuously stirred 100.0 ml aliquot of sample. Titrant addition was achieved through use of a peristaltic pump, the addition rate having been previously calibrated. Progress of the titration was followed by constantly monitoring the pH of the solution with a meter producing a recorded output. The strip-chart recorder was calibrated by determining the pen position for various buffer solutions (pH = 4.00, 7.00 and 9.00). This calibration procedure was carried out after every three samples to ensure that meter drift was not a problem. All titrations werecarried out under a continuously flushed atmosphere of inert gas (either N_2 or He) in order to prevent the absorption of CO_2 during the acidity titration. The titrations were allowed to proceed to pH >9 for acidity determinations and pH <4 for alkalinity determinations. The acidity titrations were repeated with an aliquot that was bubbled with N_2 or He for at least 10 min. prior to titration.

From the charts, the following information was calculated.

Acidity Titrations

a) Total Acidity from the amount of NaOH required to raise the sample pH to 9.00

b) Carbonate Acidity from the difference between (a) above and that obtained for a CO_2 degassed sample.

c) Free Acidity from the initial pH; free acidity = 10^{-pH}

d) "Weak Acid" Acidity from the difference between the total acidity and the sum of carbonate acidity and free acidity (a-b-c).

Titration of strong acid solutions will still show a significant "weak acid" component due to the NaOH required to raise the pH from their equivalence pH)i.e. 7) to pH = 9.00 (i.e. for the deprotonation of water). Acidity values were thus corrected for this component which is most significant for samples of very low acidity (correction is ≈ 15 μeq^{-1}).

Alkalinity Titrations

a) Total Inflection-Point Alkalinity was calculated as the amount of standardized acid titrant required to lower the sample pH to the bicarbonate-carbonic acid equivalence point.

b) Total Fixed-Endpoint Alkalinity was calculated as the amount of acid titrant required to lower the sample pH to 4.5.

RESULTS AND DISCUSSION

There are three factors indicating that a potentially serious acid rain problem exists in south-central Ontario:

1) the chemistry of precipitation in the area,

2) the low and perhaps declining buffering capacity of some of the lakes,

3) low pH and alkalinities measured in runoff from a few small watersheds.

Pertinent points regarding the three factors are outlined below:

Precipitation chemistry

a) On-Shield vs Off-Shield locations - The pH and sulphate concentrations of both precipitation events and bulk samples collected at eleven sites (Fig. 1) for varying time periods between May 1976 and April 1977 are summarized in Table 1. The first eight stations are located in the Precambrian Shield in four counties of south-central Ontario, while the last three are located either just off the Shield or on its boundary with areas of Paleozoic bedrock to the south and east. The averages given represent between 10 and 36 samples for any one station. The mean pH (mean volume-weighted hydrogen ion concentration in eq l^{-1} converted to its negative logarithm) of bulk samples varied between 4.06 and 4.22 (87-60 μeq l^{-1}) at the eight sampling locations on the Precambrian Shield, while the range of means was 4.78 - 5.79 (17-2 μeq l^{-1}) at the three stations on the Shield periphery. Ranges of pH at individual stations also were quite different at the three off-Shield stations; all eight Shield stations had individual bulk samples with pH well under 4.0 (up to 460 μeq l^{-1}), while the remaining three had no bulk samples of pH <4.0 (minimum 4.12). For the Shield stations, a total of 24 bulk samples out of 86 (28%) had pH <4.0.

The mean pH of event samples at the six Shield stations with appropriate collectors varied from 3.95 to 4.38 (138 - 42 μeq l^{-1}). However, the Dorset station, with the only winterized event collector, had a low mean pH (3.95) which reflects several very low event pH's (minimum 2.97) measured in the winter of 1976-77. As described previously, all other event collectors were not operable under freezing conditions. Excluding the Dorset station, the range of means is reduced to 4.17 - 4.38 (68-42 μeq l^{-1}), with 15 of 63 (24%) event samples having pH <4.0. Mean event pH at the three off-Shield stations, however, varied between 4.35 and 4.42 (45-38 μeq l^{-1}). These results can be summarized as follows:

1) for all six stations on the Shield with both event and bulk collectors, the mean pH of the bulk samples was lower than that of the event samples, while for the three stations (Sibbald Park, Madoc, Silver Lake) not on the Shield, the converse was true,

2) the mean pH's of event samples at the six Shield stations were only slightly different from those of the three off-Shield stations, while the mean pH's of bulk samples from eight Shield stations were much lower than those of bulk samples from the three remaining stations.

Table 1. Volume-weighted hydrogen ion (as pH and $\mu eq\ l^{-1}$) and $SO_4^{=}$ concentrations ($mg\ l^{-1}$ and $\mu eq\ l^{-1}$) in bulk and event precipitation samples at 8 stations on the Precambrian Shield in south-central Ontario and 3 stations to the south and east. The number of samples (n) and the period of collection are given. The mean pH was calculated as negative logarithm of the volume-weighted arithmetic mean H^+ concentration. The pH's in brackets were calculated as the volume-weighted arithmetic mean pH.

Station	Fraction	Period	n	H^+ pH mean	H^+ pH range	H^+ $\mu eq\ l^{-1}$	$SO_4^{=}$ $mg\ l^{-1}$	$SO_4^{=}$ $\mu eq\ l^{-1}$
1. Carnarvon	bulk	Aug'76-May'77	12	4.06(4.16)	3.64-5.87	87	4.1	85
	event	Sept'76-Oct'76	4	4.19(4.19)	4.15-4.26	64	3.7	76
2. Eagle Lake	bulk	Aug'76-May'77	9	4.17(4.27)	3.91-4.76	68	3.3	69
	event	Aug'76-Sept'77 +May'77	5	4.27(4.28)	4.10-4.40	53	3.3	69
3. Vankoughnet	bulk	July'76-Mar'77	14	4.15(4.20)	3.78-4.66	71	3.3	68
	event	April'76-Sept'76	16	4.30(4.60)	3.93-7.70	50	2.6	54
4. Gullfeather	bulk	Aug'76-Mar'77	10	4.22(4.45)	3.83-5.32	60	2.6	53
5. Dorset	bulk	Nov'76-Apr'77	16	4.12(4.27)	3.34-5.80	76	3.0	63
	event	Nov'76-Apr'77	20	3.95(4.42)	2.97-5.93	113	2.4	50
6. Red Chalk	bulk	Aug'76-May'77	9	4.14(4.17)	3.80-4.40	73	2.7	57
	event	July'76-Sept'76	10	4.17(4.24)	3.92-4.73	67	3.3	70
7. Harp Lake	bulk	June'76-Oct'76	6	4.17(4.24)	3.69-4.36	68	1.5	31
	event	June'76-Oct'76	9	4.38(4.45)	4.07-5.36	42	2.7	56
8. Harp Raft	bulk	Aug '76-Mar'77	10	4.11(4.15)	3.79-4.46	78	3.2	67
9. Sibbald Park	bulk	July'76-Sept'76	5	4.78(4.82)	4.12-6.28	17	-	-
	event	May'76-Sept'76	13	4.42(4.75)	3.93-6.89	38	3.5	72
10. Madoc	bulk	Sept'76-Oct'76	2	5.79(5.89)	5.50-6.21	2	-	-
	event	May'76-Oct'76	9	4.35(4.78)	3.98-6.71	45	3.7	77
11. Silver Lake	bulk	July'76-Oct'76	8	5.35(6.00)	4.84-6.70	5	2.5	52
	event	July'76-Sept'76	8	4.37(4.63)	4.03-6.14	42	2.7	55

Table 2. Mean and range for pH of bulk precipitation at 7 stations (12-18) surrounding our study area investigated by Kramer (1975) in 1973-75, at station (19) in Killarney Park investigated by Beamish (1977), and at 6 stations (20-25) in the Sudbury vicinity investigated as part of this study. Numbers refer to Fig. 1, n = number of samples.

Station	n	pH		H^+
		mean	range	μeq l^{-1}
12 Killarney	14	4.06	3.81-7.11	87
13 Sparrow Lake	14	4.22	3.80-5.45	60
14 Lake St. Peter	16	4.04	3.70-5.59	91
15 Traverse Lake	16	4.02	3.66-5.23	95
16 Mattawa	16	4.11	3.84-4.38	78
17 Powassan	15	4.29	3.75-5.83	51
18 Jamot	14	4.18	3.86-6.06	66
19 Lumsden Lake bulk	17	4.4	4.1 - 5.3	40
event	17	4.4	3.7 - 5.5	40
20 Nelson Lake	9	4.54[a](4.82)[b]	4.2 - 5.8	29
21 Mountaintop Lake	6	4.33(4.37)	4.2 - 4.9	47
22 Lohi Lake	15	4.21(4.27)	3.8 - 4.5	62
23 Hannah Lake	13	4.20(4.23)	3.9 - 4.8	63
24 Middle Lake	15	4.33(4.60)	3.9 - 6.3	47
25 Kelly Lake	14	4.43(4.52)	4.0 - 4.9	37

[a] calculated as volume-weighted arithmetic mean of hydrogen ion concentration (eq l^{-1}) converted to its negative logarithm.

[b] calculated as volume-weighted arithmetic mean of pH.

The above factors indicate that while there is acid rain throughout southcentral Ontario, the acidity of events may be slightly higher in the Muskoka-Haliburton region than in areas to the south and east. The acidity of bulk samples, however, is much higher in samples collected on the Shield (overall mean pH = 4.14, or 72 μeq l^{-1}) than off of the Shield (overall mean = 5.31 or 5 μeq l^{-1}). This probably indicates that entrainment of particulate matter in Paleozoic regions provides some neutralizing capacity to precipitation samples. On the other hand, in Precambrian regions there is either no entrainment from the exposed bedrock or entrainment of particles providing little, if any, buffering capacity. This may also explain the slightly higher pH's of event samples in Paleozoic regions.

Sulphate levels generally varied between 2 and 4 mg l^{-1} (42-83 μeq l^{-1}) with individual samples having up to 12 mg l^{-1} (250 μeq l^{-1}). All stations had at least one sample in the 6-8 mg l^{-1} range. The average sulphate concentrations on an equivalent basis were, in most cases, very close to the mean free hydrogen ion content measured at the stations. We do not have a sufficient number of nitrate, chloride and ammonium analyses to attempt an ionic balance (Cogbill and Likens 1974, Granat 1972) for the purpose of proportioning the acidity between different chemical species.

b) Comparison with other studies - Other works have investigated the acid nature of precipitation in south-central Ontario. Nicholls and Cox (1977) measured the pH of 14 bulk samples in 1974 at Harp Lake; their mean pH of 3.96 is in close accord with our results. Table 2 summarizes bulk precipitation data collected by Kramer (1975b) in the period 1973-75 at seven locations (Stations 12-18) surrounding our study area and by Beamish (1977) at Lumsden Lake (Station 19) in Killarney Park in 1972-73. We have also included data collected at six locations (Stations 20-25) in the Sudbury region where we have employed bulk precipitation collectors. Our measured pH's in the Sudbury region are very close to those measured by Beamish 3-4 years earlier at Lumsden Lake. However, the pH's of our eight bulk precipitation stations on the Precambrian Shield south-east of Sudbury averaged between 60 and 87 μeq H^+ l^{-1} with an overall mean (73 μeq l^{-1}) that was 50% higher than our Sudbury stations and almost identical to Kramer's (1975b) monthly bulk sample means measured 1-3 years earlier in the surrounding area.

c) Strong acid vs weak acid - There has been controversy recently over whether acidic rain is the result of a solution of weak acids or a dilute solution of strong acids (Likens and Bormann 1974, Galloway, Likens and Edgerton 1975, Table 3. pH and acidity of 4 precipitation events at the Dorset station. Two of the events were fractionated.

Date	Fraction	pH	Acidity (μeq l^{-1})					
			total	free	%	carbonate	%	"weak-acid"	%
March, 1977 (snow)	1	4.18	150	60	40	20	13	70	47
June 2, 1977	1	4.36	85	44	52	23	27	18	21
May 18, 1977	1	3.66	393	219	56	4	1	170	43
	2	3.78	305	166	54	1	<1	138	45
	3	3.76	314	174	55	<1	<1	140	45
	4	3.72	325	191	59	<1	<1	132	41
	5	3.45	583	355	61	<1	<1	228	39
	overall[a]	3.69	355	202	57	1	<1	152	43
June 1, 1977	1	3.70	340	200	59	51	15	89	26
	2	4.05	165	89	54	32	19	44	27
	3	4.15	157	71	45	20	13	66	42
	4	4.04	205	91	44	37	18	77	38
	5	4.69	85	20	24	39	46	26	30
	6	5.28	41	5	12	19	46	17	41
	7	4.98	96	10	10	22	23	64	67
	8	4.91	77	12	16	36	47	29	38
	9	4.36	85	44	52	23	27	18	21
	overall[a]	4.26	132	55	42	30	23	47	35

[a] volume-weighted

Frohlinger and Kane 1975). By comparison of free hydrogen ion concentration with total acid on four recently collected event samples (Table 3), we have demonstrated that a significant proportion of the total acidity (40-60%) is associated with strong acids. Galloway _et_ _al_. reported that 50-83% of acidity in precipitation at Ithica, 89-102% at Hubbard Brook, and 80-86% in the Adirondack Mountains, New York, was in the free state. If we subtract the carbonic acid acidity from the total acidity as Galloway _et_ _al_ propose, then 46-71% of the total acidity of the four events was accounted for by free acidity. These results support the contention of Galloway _et_ _al_ (1975) and Likens and Bormann (1974) that the low pH of precipitation is due to the presence of strong mineral acids.

d) Sources - The source of the acidity in precipitation falling on south-central Ontario is not easy to determine. The major industrial urban areas to the south and south-west in Canada and the United States are sources of nitrogen and sulphur oxides. Major sources of sulphur dioxide from smelting operations are located north and north-west of the study area. Long range atmospheric transport is such that both of these sources likely impact on the study area. The relative significance of the two possible sources is not known at this time. Lafleur and Whelpdale (1977) measured atmospheric SO_4 levels over central Ontario in August 1976 and found that highest levels were associated with southerly regional air flow, indicating that the problem may be an extension of the northeastern U.S.A. problem indentified by Likens (1976).

Further studies are underway by the Ministry of the Environment to define the principal sources of the acidity of the rainfall in this area.

Lake Chemistry

a) Buffering Capacity - The low mineral content of most lakes in south-central Ontario is well known (Ryder 1964, Sparling and Nalewajko 1970, Schindler and Nighswander 1971). Ryder demonstrated that total alkalinity (measured to a pH of 4.5) was generally <500 μeq l^{-1} with the lowest values in the 120-200 μeq l^{-1} range, while Sparling and Nalewajko measured values as low as 70-100 μeq l^{-1} in 1964. As part of a study of the water chemistry of fifteen lakes on the Precambrian Shield, we have routinely measured total fixed-endpoint alkalinities of fifteen lakes (Table 4) as a crude indication of the lakes' buffering capacities. Levels range between 95 and 195 μeq l^{-1} except for Glen Lake, a small lake situated in a pocket of Precambrian sediments with a high calcium and magnesium carbonate content. The total fixed-endpoint alkalinities averaged 129 and 143 μeq l^{-1} in the non-stratified and stratified periods. The total inflection-point alkalinities were measured on one occasion for four lakes; the resulting buffering capacities

Table 4. Location, mean total fixed endpoint alkalinity, pH[a], sulphate concentration and calcite saturation index (CSI) for the whole lake in the non-stratified period and the epilimnion during the stratified period for 15 Haliburton-Muskoka lakes. Alkalinity and CSI values in brackets are based on total inflection point alkalinity measurements.

Lake name	Latitude (°N)	Longitude (°W)	alkalinity (µeq l^{-1})		pH		SO_4 (µeq l^{-1})		CSI	
			non-stratified	epilimnion	non-stratified	epilimnion	non-stratified	epilimnion	non-stratified	epilimnion
Blue Chalk	45°12'	78°56'	134	147(70)	6.48	6.72	158	156	3.54	3.28(3.59)
Red Chalk	45°11'	78°56'	135	142(60)	6.30	6.76	152	151	3.72	3.26(3.63)
Jerry	45°23'	79°06'	137	168	6.34	6.72	219	178	3.57	3.12
Harp	45°23'	79°08'	137	152	6.24	6.70	186	180	3.72	3.22
Chub	45°13'	78°59'	107	112(30)	5.98	6.04	185	171	4.12	4.09(4.66)
Dickie	45°09'	79°05'	95	117(20)	5.69	5.91	169	167	4.55	4.21(5.05)
Basshaunt	45°07'	78°28'	195	180	6.71	7.27	182	164	2.96	2.50
Bigwind	45°03'	79°03'	112	130	6.29	6.71	164	164	3.81	3.33
Buck	45°24'	78°59'	145	160	6.26	6.89	158	167	3.66	3.01
Crosson	45°02'	79°05'	100	111	5.76	6.03	172	163	4.47	4.15
Glen	45°07'	78°28'	1190	1050	7.14	8.25	544	484	1.04	0.03
Gullfeather	45°01'	79°06'	136	112	5.97	6.11	170	167	4.07	4.03
Little Clear	45°24'	79°00'	175	195	6.45	6.88	177	157	3.32	2.93
Solitaire	45°23'	79°00'	130	160	6.56	6.86	156	159	3.46	3.05
Walker	45°23'	79°05'	130	153	6.74	6.74	180	162	3.25	3.18

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[a] Arithmetic mean

were much lower than those measured to a pH endpoint of 4.5, being between only 17 and 48% of the latter. That the inflection point of the titration curve was at pH 5.0 - 5.5 rather than 4.5 is not surprising in view of the very dilute nature of the lakes. The consequence of this, however, is that most of the available data for lakes in this region overestimate the lakes' capabilities for assimilating acidic rain.

Of the 15 lakes identified in Table 4, data collected earlier than 1976 are available for three. Nicholls (1976) reported that both Harp and Jerry Lakes had total fixed endpoint alkalinities averaging ≈ 140 μeq l^{-1} in 1973, not different from those that we have measured in 1976. Unpublished Walker Lake data collected in 1974, however, indicated ≈ 180 μeq l^{-1}, while Michalski (1971) reported an average of 400 μeq l^{-1} in 1971, based on several samples taken on a single date. If the latter figure is accurate, there has been a very significant decline in buffering capacity in Walker Lake between 1971 and 1976.

Clear Lake (Schindler and Nighswander 1971) was thoroughly investigated in 1967. Total inflection-point alkalinity was reported as 33 μeq l^{-1}. We have recently resampled Clear Lake (June 1977) and measured only 14 μeq l^{-1}. The very low drainage basin area : lake area ratio (1.4) reported for this lake may explain the very low buffering capacity, since precipitation directly on the lake's surface must be much more important relative to runoff than is usual for lakes in this region.

An alternate expression of the pH-alkalinity relationship in lakes is the calcite saturation index (Conroy, Jeffries and Kramer 1974, Kramer 1975a) which is the logarithm of the degree of saturation of a water body with respect to $CaCO_3$, where saturation yields a CSI of 0. Kramer identified a CSI of three as the level below which lakes would be generally stable relative to acid precipitation, while those with CSI between four and six would be definitely unstable to acid loadings. As shown in Table 4, four of the 15 lakes fall into the latter category, while an additional nine (CSI between three and four) can be considered possibly unstable. The only lakes with CSI <3 are Glen and Basshaunt which are situated either completely or partially on sedimentary deposits. When the inflection-point alkalinities were used for calculation of the CSI for four lakes, the CSI of each increased substantially indicating that the fixed endpoint alkalinity overestimates the buffering capacity of low ionic strength lakes.

Without detailed information about the buffering capacity (or cation exchange capacity) of the overburden in a lake's watershed, it is impossible to determine the time needed to exhaust the watershed's neutralizing capabilities (McFee, Kelly and Beck 1975). Calculations based on the capability of a lake itself are possible. A mean H^+ content of 70-100 $\mu eq\ l^{-1}$ in 1.0m of precipitation results in a loading of 70-100 meq H^+ $m^{-2}yr^{-1}$. A lake with buffering capacity of 50 $\mu eq\ l^{-1}$ and a mean depth of 10m has 500 meq m^{-2}, enough to last 5-7 years. Present buffering capacity, mean depth, and watershed area to lake surface area ratio are all important factors that will determine the eventual effects of acid rain on each lake.

b) Trace contaminants - The acidic lakes in the Sudbury region studied by Conroy et al (1975), Scheider and Dillon (1976) and Hutchinson and Stokes (1975), as well as those to the SW (Beamish 1975, 1976, Beamish and Van Loon 1977) are all characterized by elevated heavy metal concentrations, particularly of copper, nickel and zinc. Heavy metal data (Cu, Ni, Zn, Mn) for 14 of the Haliburton-Muskoka Lakes are summarized in Table 5, along with data for four Killarney Lakes and 102 Experimental Lakes Area (ELA) lakes which Beamish (1976) used to represent background levels. The Haliburton-Muskoka lakes have higher concentrations than the ELA lakes of all four metals and higher copper levels than even the Killarney Lakes. Because there are no historic heavy metal data for these lakes or any other lake in south-central Ontario it is impossible to uniquely interpret these results; they may represent natural levels in the area, elevated levels resulting from atmospheric deposition of metals, or elevated levels resulting from increased mobilization of metals from terrestrial watersheds because of the acidic nature of precipitation. In any case, these data will serve to define present levels in these lakes. We are currently measuring heavy metal levels in precipitation samples collected in the area.

Stream Chemistry

Mean pH and sulphate concentration of the inflows to two of the study lakes are summarized in Table 6. One of four inflows to Red Chalk Lake had a mean pH <4.5 while five of eight to Dickie Lake had mean pH <5.0, three being <4.5 (three additional inflows, Dickie 4, 7 and 9 are ephemeral). It is possible that these low pH's are natural since Sphagnum bogs common to the area are known to increase the acidity of their habitat (Clymo 1967),

Table 5: Mean copper, nickel, zinc and manganese concentrations in epilimnia of 14 south-central Ontario lakes in 1976. Mean levels for 4 Killarney lakes and 102 Experimental Lakes Area lakes (reported in Beamish 1976) are given for comparison

Lake		Cu	Ni	Zn (ppb)	Mn
Blue Chalk		8	1	8	44
Red Chalk		6	3	11	39
Jerry		5.5	3.5	13	115
Harp		3	3	12	40
Chub		1	0.5	12	46
Dickie		12	3	17	46
Basshaunt		9	3	15	71
Bigwind		4	3	11	30
Buck		8	3	9	41
Crosson		3	4	12	41
Gullfeather		3	5	13	57
Little Clear		10	16	19	-
Solitaire		3	0.5	-	18
Walker		4	3	12	-
	mean	5.7	3.6	12.6	49
Killarney (4 lakes)		2-4	8-12	24-36	220-260
ELA (102 lakes)		2	<3	<1	3

Table 6. Mean pH and SO_4 concentration of inflows to 2 lakes in 1976. Averages represent between 10 and 40 sampling dates.

Stream	pH[a]	SO_4 (μequ l^{-1})
Red Chalk 1	6.05	158
Red Chalk 2	4.46	238
Red Chalk 3	6.24	151
Red Chalk 4	6.22	148
Dickie 1	5.20	200
Dickie 2	5.34	252
Dickie 3	4.15	275
Dickie 5	4.53	194
Dickie 6	4.42	242
Dickie 8	5.30	233
Dickie 10	4.72	233
Dickie 11	4.20	269

[a] arithmetic mean of pH

Golterman 1975). However, the possibility that these streams may drain watersheds whose buffering capacities have been depleted by acidic precipitation cannot be ignored. The measured pH's of these streams are lower than any others previously measured in the area, including those directly draining Sphagnum bogs (Sparling, pers. comm.). We are presently undertaking a detailed geochemical survey of these watersheds.

SUMMARY AND CONCLUSIONS

Recent investigations have shown that precipitation in south-central Ontario is typically of pH 3.9 - 4.4 identical to that measured by Likens et at (1975) in the northeastern U.S.A. (mean annual pH at Hubbard Brook ranged from 4.03 to 4.21 between 1970-74) and lower by 0.1 - 0.2 units than now reported for Scandanavia (Dovland, Joranger and Semb 1976). The acidity of precipitation as measured by bulk samples in south-central Ontario in 1976 was 50% greater than that in the Sudbury region and identical to that previously reported by Kramer (1975b) around our study area. On Precambrian bedrock, bulk precipitation samples had lower pH than event samples, suggesting that entrained particulate matter, if present, provided no buffering capacity, while the converse was true for sites located in calcareous regions. At least 25% of the precipitation events of 1976 had pH <4.0 with a minimum value of 2.97 measured during one snowfall. Between 40 and 60% of the total acidity of precipitation was characterized as strong acid.

Available information relevant to sources of this acidity is scarce but contributions from smelting operations to the N and NW and large urban areas to the SE-SW are probable.

The buffering capacity of most of the lakes in south-central Ontario is extremely low (13-200 μeq l^{-1}). Because the bedrock and overburden of most of the region is very sparingly soluble and provides little buffering, acidification of lakes and streams is likely. An estimation of the time required for this to happen is not possible, but there is already a small amount of evidence suggesting declining buffering capacity in a few lakes. Heavy metal (Cu, Ni, Zn, Mn) levels in lakes of the region are higher than in lakes in another Precambrian area receiving little or no atmospheric inputs of industrial origin and are approaching levels found in lakes in Killarney Park, south-west of Sudbury.

The pH of the runoff from several small watersheds averaged <5.0 with four having runoff of pH <4.5 over 1976. There is at least a possibility that this reflects depletion of watershed buffering capacity.

The potential effects of acidic precipitation on Ontario are extremely serious; both aquatic and terrestrial damage have been documented in other parts of the world (e.g. Abrahamsen et al 1976, Odén 1975, Gorham 1975, Odén and Ahl 1970, Almer et al 1974 etc.) Because a large portion of Ontario is underlain by Precambrian bedrock, the region that can possibly be affected is large. There is no doubt that should current acid loadings continue in south-central Ontario, the acidification of a large number of lakes and streams will follow.

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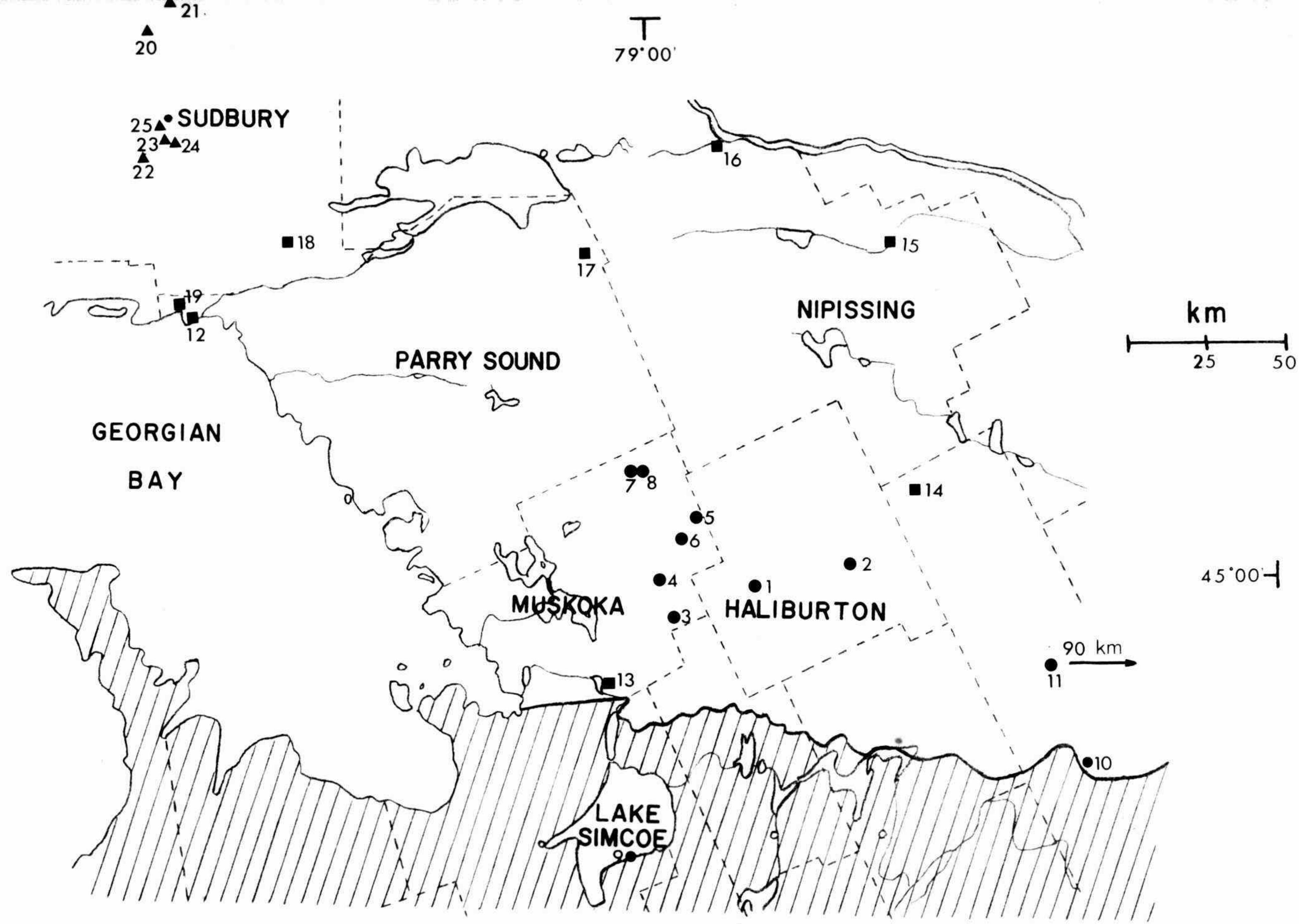
List of Figures

Fig. 1. Location of precipitation collection sites. Shaded area is Paleozoic bedrock, clear area is Precambrian. Station numbers refer to Tables 1 and 2.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